

JAPANESE

[JP,2003-073542,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM
MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polyamide resin composition which is excellent in a mechanical strength especially creep resistance, and surface appearance.

[0002]

[Description of the Prior Art] Conventionally, in order to improve the mechanical properties of polyamide resin, blending glass fiber and an inorganic bulking agent with resin is carried out. However, there is a problem that shock resistance is low and that distribution of the inorganic filler in resin and interface adhesion are bad, and surface appearance is bad only by carrying out melt kneading of these inorganic fillers simply. Then, in order to heighten the compatibility or associative strength of thermoplastics and an inorganic filler, perform coupling processing of an organic silane compound etc. on the surface of an inorganic filler, and there is a method of improving the filler distribution in resin, but. By this method, it is a grade which improves familiarity between resin and an inorganic filler, and has not resulted in sufficient improvement. In order to obtain sufficient intensity, the fill ration needed to be raised in the usual filler, and the problem that the resin composition obtained becomes high specific gravity is also produced.

[0003]Although the use as a filler was tried for many years, the secondary aggregation occurred in the usual mixing and kneading, and uniform distribution into resin was difficult for the argillite which is a kind of an inorganic laminar compound on the other hand. The trial which makes uniform distribution profitably like by using the intercalation compound which makes a sheet silicate JP,8-12881,A with a host, and makes a guest the specific fourth class ammonium ion is made. After swelling argillite with a solvent to JP,8-151449,A or JP,9-48856,A, melt kneading is carried out to resin, and the trial which removes a solvent by holding to decompression the vent-port provided in the extrusion machine, and makes uniform distribution profitably like is indicated.

[0004]

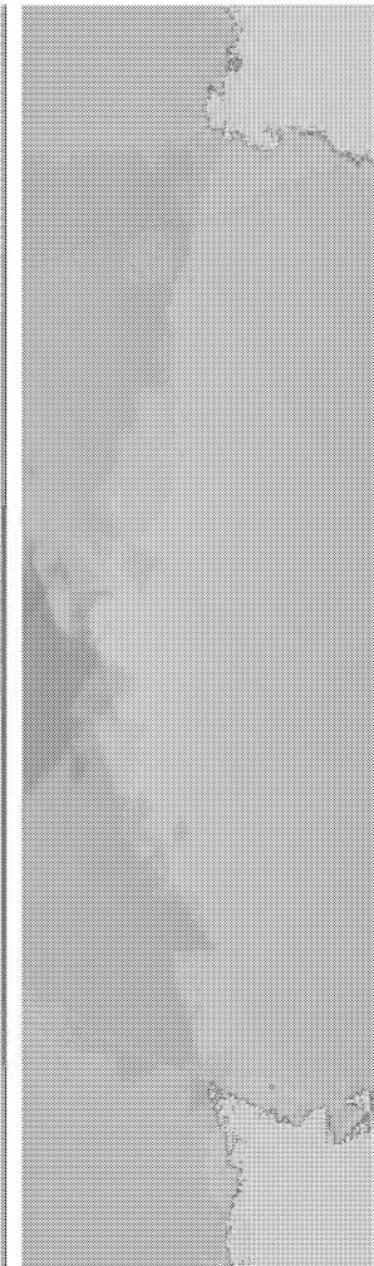
[Problem(s) to be Solved by the Invention]Although what is necessary is to have found a certain amount of improvement in mechanical properties, such as intensity and an elastic modulus, and just to have increased the addition of the sheet silicate with such art in order to obtain higher rigidity, there was a problem as which the fall of a moldability and the fall of surface appearance are regarded in connection with it.

[0005]An object of this invention is to obtain the polyamide resin composition which has high mechanical strength, especially creep resistance without reducing surface appearance.

[0006]

[Means for Solving the Problem]In order that artificers may solve an aforementioned problem, as a result of repeating examination wholeheartedly, polyhexamethylene adipamide to polyamide made into a main constituent. A compound chosen from a swelling sheet silicate, a copper compound, fatty acid amide, fatty acid, and its derivative and a polyamide resin composition which blends higher-fatty-acid metal salt found out that an aforementioned problem was solvable, and resulted in this invention.

[0007]Namely, this invention receives polyamide 100 weight section which makes (1) and (A) polyhexamethylene adipamide a main constituent, (B) 0.05 to swelling sheet silicate 30 weight section, the (C) copper compound 0.001 - 0.5 weight section, (D) 0.01 to compound 0.5 weight section chosen from among aliphatic series amide, fatty acid, and its derivative, (E) A polyamide resin composition containing 0.01 to higher-fatty-acid metal salt 0.5 weight section, and further this invention, (2) A polyamide resin composition of the aforementioned (1) statement, wherein the (C) copper compound is a univalent copper halide compound. The above (1), wherein a compound of (3) and (D) is aliphatic series amide, or a polyamide resin composition given in (2), (4) -- either of aforementioned (1) - (3), wherein (E) higher-fatty-acid metal salt is metal stearate -- (5) aforementioned (1) either a polyamide resin composition of a statement or - (4) -- mold goods which fabricate a polyamide resin composition of a statement are considered as composition.



[0008]

[Embodiment of the Invention] This invention is explained in detail below. the polyamide resin which makes a main constituent (A) polyhexamethylene adipamide used by this invention uses hexamethylenediamine and adipic acid as a main raw material -- at least -- more than 50 mol % -- the polycondensation body which has an amide bond produced by using is said. To polyamide resin of this invention, a little other copolymerization ingredients may be added in the range which does not spoil the purpose of an invention. As a typical example of the copolymerization ingredient, 6-aminocaproic acid, 11-aminoundecanoic acid, Amino acid, such as 12-amino dodecanoic acid and paraamino methylbenzoic acid, Lactam, such as epsilon caprolactam and omega-RAURO lactam, a tetramethylenediamine, 2-methyl pentamethylene diamine, undecamethylene diamine, dodecamethylenediamine, (2,2,4- or 2,4,4-) Trimethyl hexamethylenediamine, 5-methyl nonamethylene diamine, meta-xylylene diamine, PARAKI silylenediamine, 1,3-bis(aminomethyl) cyclohexane, 1,4-bis(aminomethyl)cyclohexane, The 1-amino-3-aminomethyl 3 and 5, 5-trimethylcyclohexane, Bis(4-aminocyclohexyl) methane, bis(3-methyl-4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, a bis(aminopropyl)piperazine, Aliphatic series, such as an aminoethyl piperazine, alicycle fellows, aromatic diamine and SUPERIN acid, azelaic acid, sebacic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, 2-chloroterephthalic acid, 2-methylterephthalic acid, Aliphatic series, such as 5-methylisophthalic acid, 5-sodium sulfoisophthalate, hexahydro terephthalic acid, and hexahydro isophthalic acid, alicycle fellows, aromatic dicarboxylic acid, etc. are mentioned.

[0009] It is also possible to mix and use a small amount of other polyamide resin for polyhexamethylene adipamide resin (Nylon 66 resin) as polyamide of this invention. As polyamide resin which can be mixed and used, PORIKA pro amide (nylon 6), PORIKA pro amide / polyhexamethylene adipamide copolymer (nylon 6/66), Polytetra ethylene adipamide (Nylon 46), polyhexamethylene sebacamide (Nylon 610), Polyhexamethylene DODEKAMIDO (Nylon 612), polyhexamethylene terephthalamide / PORIKA pro amide copolymer (nylon 6 T/6), Polyhexamethylene terephthalamide / polydodecane amide copolymer (nylon 6 T/12), Polyhexamethylene adipamide / polyhexamethylene terephthalamide copolymer (Nylon 66 /6T), Polyhexamethylene adipamide / polyhexamethyleneisophthalamide copolymer (Nylon 66 /6I), Polyhexamethylene adipamide / polyhexamethyleneisophthalamide / PORIKA pro amide copolymer (Nylon 66 /6I/6), Polyhexamethylene adipamide / polyhexamethylene terephthalamide / polyhexamethyleneisophthalamide copolymer (Nylon 66 /6T/6I), Polyhexamethylene terephthalamide / polyhexamethyleneisophthalamide copolymer (nylon 6 T/6I), Polyhexamethylene terephthalamide / poly(2-methyl pentamethylene) terephthalamide copolymer (nylon 6 T/M 5T), Polyhexamethylene

terephthalamide / polyhexamethylene sebacamide / PORIKA pro amide copolymer (nylon 6 T/610/6), Polyhexamethylene terephthalamide / polydodecane amide / polyhexamethylene adipamide copolymer (nylon 6 T/12/66), Polyhexamethylene terephthalamide / polydodecane amide / polyhexamethyleneisophthalamide copolymer (nylon 6 T/12/6I), polyxylylene adipamide (nylon XD6), etc. are mentioned.

[0010] Although there is no restriction in particular in the degree of polymerization of this polyamide resin, the thing of the range of 2.0-7.0 is preferred as relative viscosity measured at 25 ** among 1% of the weight of a 98% concentrated-sulfuric-acid solution.

[0011] With (B) swelling sheet silicate used by this invention. "Clay handbook" Although shown in p.41-43 (edited by Clay Science of Japan, Gihodo Shuppan Co., Ltd. (January 15, Showa 42 issue)), **** aluminum, It has a 2:1 type structure which a silicic acid tetrahedron sheet laps with the upper and lower sides of the octahedron sheet containing the element chosen from magnesium, lithium, etc., and forms the plate crystal layer of one sheet, and has a positive ion of convertibility between the layers of the plate crystal layer. The sizes of the plate crystal of one sheet are usually 0.05-0.5 micrometer in width, and 6-15 Å in thickness. It is desirable still more preferred to use a 20 to 300 meq/100 g thing, and the cation exchange capacity of the exchangeable cation is a thing of the range of 80 to 150 meq/100 g.

[0012] As an example of this sheet silicate, montmorillonite, beidellite, Smectite system argillite, such as nontronite, saponite, hectorite, and a saconite, A vermiculite, halloysite, a money dynamite, Kenya Ito, zirconium phosphate, Fluoride mica of swelling nature, such as various argillite, such as phosphoric acid titanium, Li type fluoride TENIO light, a Na-type fluoride TENIO light, Na-type 4 silicon fluoride mica, and Li type 4 silicon fluoride mica, etc. are mentioned, and it may be a natural thing or may be compounded. Fluoride mica of swelling nature, such as smectite system argillite, such as montmorillonite and hectorite, Na-type 4 silicon fluoride mica, Li type fluoride TENIO light, is preferred also in these, and it is more preferred to use smectite system argillite, such as montmorillonite.

[0013] It is preferred to use for (B) swelling sheet silicate of this invention the sheet silicate which contains organic onium ion between the layers of a plate crystal layer.

[0014] As organic onium ion, ammonium ion, phosphonium ions, sulfonium ion, etc. are mentioned. In these, ammonium ion and phosphonium ions are preferred, and especially ammonium ion is fond and is used. As ammonium ion, they may be any of first-class ammonium ion, the second class ammonium ion, the third class ammonium ion, and the fourth class ammonium ion.

[0015] For example, as first-class ammonium ion, decyl ammonium, dodecyl ammonium, octadecyl ammonium, oleyl ammonium, benzylammonium, etc. are mentioned.

[0016] Methylidodecyl ammonium, methyloctadecyl ammonium, etc. are mentioned as the second class ammonium ion.

[0017]Dimethyldodecyl ammonium, dimethyloctadecyl ammonium, etc. are mentioned as the third class ammonium ion.

[0018]As the fourth class ammonium ion, benzyl trimethylammonium, Benzyl triethyl ammonium, benzyl tributyl ammonium, Benzyl trialkyl ammonium ion, such as benzylidemethyldodecyl ammonium and benzyl dimethyloctadecyl ammonium, Trioctyl methylammonium, trimethyl octyl ammonium, Alkyl trimethyl ammonium ion, such as trimethyl dodecyl ammonium and trimethyl octadecyl ammonium, Dimethyl dialkyl ammonium ion, such as dimethyldioctyl ammonium, dimethyldidodecyl ammonium, and dimethyldioctadecyl ammonium, etc. are mentioned.

[0019]Besides these, aniline, p-phenylene diamine, alpha-naphthylamine, The ammonium ion etc. which are derived from p-aminodimethylaniline, benzidine, pyridine, piperidine, 6-aminocaproic acid, 11-aminoundecanoic acid, 12-amino dodecanoic acid, an ethanolamine derivative, a diethanolamine derivative, etc. are mentioned.

[0020]Also in such ammonium ion, the sum total of the carbon number of the intramolecular of ammonium ion is preferred for especially the fourth class ammonium ion of 11-30. Specifically, they are trioctyl methylammonium, trimethyl octadecyl ammonium, benzylidemethyldodecyl ammonium, benzyl dimethyloctadecyl ammonium, etc.

[0021]The sheet silicate in this invention which contains organic onium ion between layers can be manufactured by making the sheet silicate and the organic onium ion which have a positive ion of convertibility between layers react by a publicly known method. The method by carrying out the direct reaction of the ammonium salt which it was liquefied to the method and sheet silicate by an ion exchange reaction in the inside of polar solvents, such as water, methanol, and ethanol, or specifically carried out melting to them, etc. are mentioned.

[0022]In this invention, from points, such as the dispersibility of a sheet silicate, thermal stability at the time of melting, gas at the time of shaping, and generation control of a bad smell, the quantity of the organic onium ion to a sheet silicate is preferred to the cation exchange capacity of a sheet silicate, and the range of it is 0.4-2.0 Eq. It is 0.8-1.2 Eq more preferably.

[0023]As for a sheet silicate, it is preferred to use it apart from making the above-mentioned organic onium salt contain by the coupling agent which has a reactive functional group, carrying out conditioning in order to obtain the more outstanding mechanical strength. As this coupling agent, an isocyanate system compound, the organic Silang system compound, an organic titanate compound, an organic borane system compound, an epoxy compound, etc. are mentioned.

[0024]Especially a desirable thing is the organic Silang system compound (it may be called a silane coupling agent below), and as the example, Gamma-glycidoxypropyltrimetoxysilane, gamma-glycidoxypyl TORIETOKISHI silane, Epoxy group content alkoxy silane

compounds, such as beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, Sulfhydryl group content alkoxy silane compounds, such as gamma-mercaptopropyltrimethoxysilane and gamma-mercaptopropyltriethoxysilane, gamma-ureido propyl triethoxysilane, gamma-ureido propyl trimethoxy SHISHIRAN, Ureido group content alkoxy silane compounds, such as gamma-(2-ureido ethyl) aminopropyltrimethoxysilane, gamma-isocyanatopropyl triethoxysilane, gamma-isocyanato propyltrimethoxysilane, gamma-isocyanato propylmethyl dimethoxysilane, gamma-isocyanato propylmethyl diethoxysilane, Isocyanato group content alkoxy silane compounds, such as gamma-isocyanatopropylethyl dimethoxyshiran, gamma-isocyanatopropylethyl diethoxysilane, and gamma-isocyanatopropyltrichlorosilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, Amino group content alkoxy silane compounds, such as gamma-(2-aminoethyl) aminopropyl trimethoxysilane and gamma-aminopropyltrimethoxysilane, Hydroxyl group content alkoxy silane compounds, such as gamma-hydroxypropyl trimethoxysilane and gamma-hydroxypropyl triethoxysilane, Carbon carbon unsaturation group content alkoxy silane compounds, such as gamma-methacryloxypropyl trimethoxy silane, vinyltrimetoxysilane, N-beta-(N-vinylbenzyl aminoethyl)-gamma-aminopropyl trimethoxysilane, a hydrochloride, etc. are mentioned. In particular, a carbon carbon unsaturation group content alkoxy silane compound is used preferably.

[0025] Processing of the sheet silicate in these silane coupling agents, A sheet silicate is added in high speed stirring and mixing machines, such as a method of making a silane coupling agent sticking to a sheet silicate in polar solvents, such as water, methanol, and ethanol, or these mixed solvents, and a Henschel mixer, The method of making it dropping and adsorbing in the form of the solution containing a silane coupling agent or an organic solvent, the method by adding a silane coupling agent directly to a sheet silicate further, and making it mix and adsorb with a mortar etc., etc. are mentioned stirring, and which method may be used. When processing a sheet silicate by a silane coupling agent, in order to promote hydrolysis of the alkoxy group of a silane coupling agent, it is preferred to mix water, acid water, alkaline water, etc. simultaneously. In order to raise the reaction efficiency of a silane coupling agent, the organic solvent which dissolves both water, such as methanol and ethanol, and a silane coupling agent other than water may be mixed. It is also possible to promote a reaction further by heat-treating the sheet silicate processed by such a silane coupling agent. When carrying out melt kneading of a sheet silicate and the thermoplastic polyester, without performing processing by the coupling agent of a sheet silicate beforehand, what is called the integral blending method that adds these coupling agents may be used.

[0026] Although there is no restriction in particular also in an order of processing by the organic onium ion of a sheet silicate, and processing by a coupling agent, after processing by organic onium ion first, it is preferred to perform coupling agent processing.

[0027]As for the content of (B) swelling sheet silicate, in this invention, it is preferred that 0.05-30 weight-section content is carried out as an inorganic ash content to polyamide resin 100 weight section of this invention. It is 0.2 to 10 weight section especially preferably 0.1 to 20 weight section more preferably. The physical-properties improvement effect is small in content being less than 0.05 weight sections, and if content exceeds 30 weight sections, toughness will fall. an inorganic ash content makes the polyamide resin composition 2g incinerate in a 500 ** electric furnace for 3 hours -- incineration -- it asks from the mass of order.

[0028]The (C) copper compounds used by this invention are a copper compound, for example, a copper halogenide, sulfate, acetate, fatty acid salt, etc. As a concrete example, a cuprous chloride, a cupric chloride, the first copper of bromination, the second copper of bromination, A cuprous iodide, the second copper of iodination, cupric sulfate, the second copper of nitric acid, copper phosphate, A complex compound with the first copper of acetic acid, the cupric acetate, the second copper of salicylic acid, the second copper of stearic acid, the second copper of benzoic acid and said inorganic-halogens-sized copper, xylylene diamine, 2-mercaptopbenzimidazole, benzimidazole, etc., etc. are mentioned. A univalent copper compound division univalent copper halide compound is preferred, and the first copper of acetic acid, a cuprous iodide, etc. can be especially illustrated as a suitable copper compound.

[0029]In the polyamide resin composition of this invention, as for the content of the (C) copper compound, it is preferred that it is 0.001 - 0.5 weight section to polyamide resin 100 weight section, and it is 0.01 - 0.5 weight section more preferably. When the content of a copper compound is less than 0.001 weight sections, there is a possibility that creep resistance may fall, and if content exceeds 0.5 weight sections on the other hand, discoloration by water absorption of a polyamide resin composition will become remarkable.

[0030]It is also possible to add an alkali halide compound in the form used together with a copper compound in this invention. As an example of this alkali halide compound, a lithium chloride, a lithium bromide, lithium iodide, potassium chloride, potassium bromide, potassium iodide, a sodium bromide, sodium iodide, etc. can be mentioned, and potassium iodide and especially sodium iodide are preferred. To this, it is preferred that it is usually the range of 0.01 to 1 weight section to polyamide resin 100 weight section, and it is preferred to it that it is especially the range of further 0.05 to 0.8 weight section.

[0031]As aliphatic series amide, the thing of the following general formula is preferably used as a compound chosen from among (D) aliphatic series amide used by this invention, fatty acid, and its derivative.

$R_2CONH-R_1(1)$

$R_4CONH-R_3-NHCOR_5(2)$

R₇NHCO-R₆-CONHR₈ (3)

R₁₀CONH-R₉-CONHR₁₁ (4)

R is a hydrocarbon group each among a formula -- desirable -- R₁ -- hydrogen or the hydrocarbon group of the carbon numbers 1-35. The hydrocarbon group of R₂, R₄, R₅, R₇, R₈, R₁₀, and the R₁₁ carbon numbers 1-35, R₃, R₆, and R₉ are the hydrocarbon groups of the carbon numbers 1-12.

R₁, R₄, R₅, R₇, R₈, As an example of R₁₀ and R₁₁, a methyl group, an ethyl group, A propyl group, an isopropyl group, n-butyl group, a pentyl group, a hexyl group, A heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a tridecyl group, A tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, an eicosanyl group, a heneicosanyl group, a docosanyl group, a tricosanyl group, a tetracosanyl group, an ethylhexyl group, etc. are mentioned.

[0032]As an example of R₃, R₆, and R₉, a methylene group, Ethylene, a trimethylene group, a tetramethylene group, a pentamethylene group, A hexamethylene group, a heptamethylene group, an octamethylene group, a nonamethylene group, a decamethylene group, an undecamethylene group, a dodecamethylene group, an isopropylidene group, a phenylene group, a xylylene group, etc. are mentioned.

[0033]As an example of said aliphatic series amide, for example Lauryl amide, milli still amide, Palmitylamide, stearylamide, AIKO sill amide, behenyl amide, Monoamide, such as oleylamide, N-stearylstearylamine, N-oleyl oleylamide, N-stearyl oleylamide, N-oleylstearylamine, Bisamide, such as substitution monoamide, such as N-oleylpalmitylamide, and also methylene-bis-stearylamine, methylenebis-oleylamide, ethylene-bis-stearylamine, ethylene bis(oleylamide), and hexa methylene-bis-stearylamine, is used suitably. Aliphatic series bisamide, such as ethylene-bis-stearylamine, is suitably used also especially in these.

[0034]Fatty acid and its derivative are ester obtained from aliphatic carboxylic acid and aliphatic carboxylic acid, and aliphatic series dihydric alcohol, its partial saponification thing, etc., As an example of carboxylic acid, lauric acid, myristic acid, Barh Myzin acid, Stearic acid nonadecanoic acid, arachidic acid, behenic acid, lignoceric acid, Cerinic acid, heptacosanoic acid, montanic acid, melissic acid, RAKUSERU acid, Oleic acid, elaidic acid, a cetoleic acid, erucic acid, brassidic acid, Linolic acid, linolenic acid, arachidonic acid, steer roll acid, etc. can be mentioned, and ethylene glycol, propylene glycol, 1, 4-butanediol, 1, 6-hexandiol, a polyethylene glycol, etc. are mentioned as an example of aliphatic series dihydric alcohol.

[0035]As an example of the derivative of said fatty acid, the montanic acid aliphatic series divalent alcohol ester of Hoechst Japan "Hoechst wax E", The ethylene glycol ester of montanic acid ester, such as a

partial saponification thing "Hoechst wax OP" of the montanic acid aliphatic series divalent alcohol ester of Hoechst Japan, and the derivative of those, and melissic acid, its derivative, etc. are used suitably.

[0036]As content of the compound chosen from these (D) fatty acid amide, fatty acid, and its derivative, it is 0.01 - 0.5 weight section to polyamide 100 weight section, and is 0.05 - 0.3 weight section preferably. When less than 0.01 weight sections, there is a possibility that surface appearance may fall, if more than 0.5 weight section, the generating gas at the time of melting of a constituent will increase, and the smooth nature on the surface of mold goods will fall by silver generating etc.

[0037]as (E) higher-fatty-acid metal salt used by this invention -- usually -- less than 25 or more 10 carbon number -- especially -- the [less than 22 12 or more fatty acid and periodic table] -- the fatty acid metal salt obtained from I-III fellows' metal is used preferably. As an example of fatty acid, stearic acid, Barh Myzin acid, oleic acid, ARAGIN acid, behenic acid, etc. can be mentioned, and zinc, calcium, lithium, aluminum, barium, potassium, magnesium, etc. can be mentioned as a metalated example.

[0038]Also in these, metal salt of stearic acid is preferred and zinc stearate, calcium stearate, lithium stearate, aluminum stearate, barium stearate, magnesium stearate, etc. are mentioned as the example.

[0039]As loadings of higher-fatty-acid metal salt, it is 0.01 to 0.5 weight section to polyamide 100 weight section, and is 0.02 to 0.3 weight section preferably. if less than 0.01 weight sections, it will see in a good screw and lump stability will not be obtained, but if more than 0.5 weight section, the generating gas at the time of melting of a constituent will increase, and the smooth nature on the surface of mold goods will fall by silver generating etc.

[0040]In the polyamide resin composition of this invention, it is preferred that the sheet silicate is distributing uniformly on the level of a monolayer in polyamide resin which is a matrix. The state where the level of a monolayer is distributing uniformly is in the state where a sheet silicate is about monolayer -10 layer, and it means distributing to the whole matrix resin, without carrying out a secondary aggregation. This state can be checked by cutting a section from a polyamide resin composition and observing this with an electron microscope.

[0041]An inorganic filler can be blended with the polyamide resin composition of this invention in order to give intensity and rigidity in addition to the sheet silicate of further above-mentioned swelling nature. As an inorganic filler, restriction in particular has neither tabular, which cylindrical and spherical un-fibrous inorganic filler nor a fibrous or needlelike inorganic filler. As a non-fibrous inorganic filler, Huaras Tena Ito, zeolite, a sericite, Kaolin, mica, clay, pyrophyllite, asbestos, talc, Silicate, such as alumina silicate, alumina, oxidized silicon, magnesium oxide. Metallic oxides, such as zirconium oxide, titanium oxide, and iron oxide, calcium carbonate, Sulfate, such as

carbonate, such as magnesium carbonate and dolomite, calcium sulfate, and barium sulfate, Hydroxide, such as magnesium hydroxide, calcium hydroxide, and aluminium hydroxide, Inorganic fillers, such as a glass bead, a ceramic bead, boron nitride, silicon carbide, and silica, may be mentioned, these may be hollow, and it is also possible to use together two or more kinds of these inorganic fillers further.

[0042]As for these inorganic fillers, it is preferred to use it by the coupling agent which has a reactive functional group, carrying out conditioning in the meaning which obtains the more outstanding mechanical strength. As this coupling agent, an isocyanate system compound, the organic Silang system compound, an organic titanate compound, an organic borane system compound, an epoxy compound, etc. are mentioned.

[0043]To the polyamide resin composition of this invention. Shock nature improvement material, such as various addition ingredients publicly known in the range which does not spoil the purpose of this invention, for example, various elastomers, Additive agents, such as antioxidants, such as a nucleus agent, coloration inhibitor, hindered phenol, and hindered amine, an epoxy compound, a plasticizer, lubricant, a weathering agent, and colorant, can be added.

[0044]There is no restriction in particular in the method of manufacturing the polyamide resin composition of this invention, (A) What is necessary is just to add the compound (E) higher-fatty-acid metal salt chosen from among the sheet silicate (C) copper compound (D) aliphatic series amide of (B) swelling nature, fatty acid, and its derivative at one after a polymerization of the times before the polymerization of polyamide resin in the middle of a polymerization. Especially a desirable method is the method of carrying out melt kneading of the compound (E) higher-fatty-acid metal salt chosen from among the sheet silicate of (B) swelling nature, the (C) copper compound, (D) aliphatic series amide and fatty acid, and its derivative after the polymerization of (A) polyamide resin. As for (E) higher-fatty-acid metal salt, it is also preferred to carry out externally adding at the time of shaping.

[0045]What is necessary is for there to be no restriction in particular in the melt kneading method, and just to be able to perform mechanical shearing under the molten state of polyamide resin. Although any of a batch type or continuous system may be sufficient also as the mode of processing, the continuous system which can be manufactured continuously is more preferred from the field of productivity. Although there is no restriction in particular also in the kneading apparatus to be used, it is preferred to use an extrusion machine, especially a twin screw extruder in respect of productivity. It is also fond to provide a vent-port in a melt kneading machine, and to draw in under decompression in order to remove the moisture generated at the time of melt kneading and the volatile constituent of low molecular weight, and it is used. In using a twin screw extruder, the sheet silicate, the (C) copper compound, and (D) aliphatic series amide of (A) polyamide

resin and (B) swelling nature, The compound and (E) higher-fatty-acid metal salt which are chosen from among fatty acid and its derivative are beforehand mixed with the blender etc., There is no restriction in particular also in the methods of supply, such as the method of supplying it from the feeding mouth of an extrusion machine, and the method of supplying the (A) ingredient and the (C) ingredient from the feeding mouth of the upstream of an extrusion machine, and supplying the (B) ingredient, the (D) ingredient, and the (E) ingredient from the feeding mouth of the downstream. Although there is no restriction in particular also in the screw arrangement of an extrusion machine, in order to make a sheet silicate micro-disperse-ize, it is preferred to provide a kneading zone.

[0046]The polyamide resin composition of this invention can be fabricated by a publicly known method, and can be used as mold goods. The polyamide resin composition of this invention may be used in the state of a masterbatch in that case. As an example, namely, some (A) polyamide resin, the sheet silicate of (B) swelling nature, the (C) copper compound, and (D) aliphatic series amide, The method of blending and carrying out melt molding of the masterbatch pellet which consists of a compound chosen from among fatty acid and its derivative and (E) higher-fatty-acid metal salt, and the pellet of the remainder of (A) polyamide resin, and using as mold goods directly, etc. are mentioned. As a forming process, publicly known forming processes, such as injection molding, extrusion molding, and blow molding, are specifically mentioned. Since the obtained mold goods are the small amount of fillers, the high rate of bending flexibility is shown and it excels especially in creep resistance, it is suitable for various engineering parts and a structural material.

[0047]As an example of the concrete use, various gears, various cases, a sensor, a connector, A socket, a resistor, a relay case switch coil bobbin, housing, The electric electronic component, VTR which are represented by the computer associated part etc., Television, an iron, a hair drier, a rice cooker, a microwave oven, audio equipment, The home represented by a light, a refrigerator, an air-conditioner, a typewriter, word processor, etc., Various bearings, such as a clerical work electric product part, oilless bearing, and stern bearing and submerged bearing, Motor part article, writer, typewriter, various bolt nut, and power-tool housing, Machinery associated parts, such as wheels, such as a bicycle, a tricycle, and a snow car, an AC-dynamo terminal, An AC-dynamo connector, an I.C. regulator, the potentiometer base for light DIYA, A fuel relation, an exhaust system, and [various valves, such as an exhaust air gas valve and] suction system various pipes, An air intake nozzle snorkel, an intake manifold, a fuel pump, Engine-cooling-water joint, carburetor main body, a carburetor spacer, an exhaust gas sensor, a cooling water sensor, an oil temperature sensor, a throttle position sensor, a crankshaft position sensor, An air flow meter, a brake bat wear sensor, the thermostat base for air-conditioners, A heating warm air flow control valve, the brush

electrode holder for radiator motors, A water pump impeller, turbine ** yne, windshield-wiper-motor relation parts, DEYUSUTORIBYUTA, a starting switch, a starter relay, a wire harness connector, A window OSSHA nozzle, an air conditioning panel switch board, the coil for fuel relation electromagnetism valves, The connector for fuses, horn terminals, an electric equipment article electric insulating plate, a stepping motor rotor, A lamp socket, a lamp reflector, a lamp housing, a brake piston, A solenoid bobbin, an engine oil filter, an ignition case, a relay box, A junction box, a wheel cap, a clip, a fastener, Furniture associated parts, such as construction materials, such as motor vehicle associated parts, such as an engine cover, a cylinder head cover, a timing belt cover, and a radiator tank, the inner package and exterior parts of a residence, a structural material, under floor support, and a sash part, and a chair leg, etc. are mentioned.

[0048]

[Example]This invention is further explained in full detail according to an example below.

The degree of polymerization of evaluation criteria and measuring-method polyamide resin: It asked among 98% concentrated sulfuric acid as relative viscosity measured by 25 ** and 1 % of the weight of concentration.

[0049]The rate of bending flexibility: It evaluated according to ASTM D790. Specimen size was used as the cylindrical specimen (1/2inchx5inchx1 / 4 inches).

[0050]Creep-property examination: The creep-under-tensile-force distortion amount of 100 hours after was measured by 100 ** and load 20MPa using the ASTM No. 1 specimen with a specimen thickness of 1/8 inch.

[0051]Surface appearance: The 80mmx80mmx3mm corner guard was fabricated by injection molding, the mold-goods surface was observed visually, and it was considered as surface appearance. The judgment copied the fluorescent lamp of the ceiling on the surface of the corner guard, and "***" and the thing as which silver and the flow mark are regarded on the mold-goods surface or it is not observed at all made "x" what the form of the fluorescent lamp can observe in the form of that in which "O" and an outline bleed what is observed clearly.

[0052]A stirred part scatters 100 g of example 1 Na-type montmorillonite (cation exchange capacity (it may abbreviate to CEC below) of 85 meq/100g) to 10 l. of warm water, 2 l. of warm water in which 36 g (it is 1.0 time to cation exchange capacity) of benzylidemethylstearyl ammoniumchloride (BDMS: carbon number 27) was dissolved was added here, and it stirred for 1 hour. Warm water washed, after a ** exception's carrying out formed precipitate. this washing and ** -- vacuum drying of the solid obtained by performing another operation 3 times was carried out at 80 **, and the dry swelling sheet silicate was obtained. It blends so that relative viscosity may serve as 0.5 weight sections with an inorganic ash content in this swelling sheet silicate at Nylon 66 resin 100 weight section of 2.9, After

blending 0.02 weight sections and potassium iodide by 0.03 weight sections and blending ethylene-bis-stearyl amide for a cuprous iodide by 0.3 weight sections and a part tumbler mixer, melt kneading of the cylinder temperature was carried out with the PCM-30 type twin screw extruder (IKEGAI) set as 280 **, and the resin composition was obtained. After adding and mixing so that vacuum drying may be carried out at 80 ** for 10 hours and it may become 0.03 weight sections to polyamide resin 100 weight section about calcium stearate at the time of shaping, after pelletizing, the obtained constituent performed injection molding with the cylinder temperature of 280 **, and the die temperature of 80 **, and obtained the specimen. The evaluation result of a mechanical physical property and surface appearance was shown in Table 1.

[0053] Except making the loadings of an example 2 swelling sheet silicate into one weight section, after carrying out melt kneading to Nylon 66, and the sheet silicate of swelling nature, a fatty acid compound and higher-fatty-acid metal salt and obtaining a resin composition like Example 1, shaping and evaluation were performed. The result was shown in Table 1.

[0054] Except making the addition of example 3 cuprous iodide into 0.05 weight sections, after obtaining a polyamide resin composition like Example 2, shaping and evaluation were performed. The result was shown in Table 1.

[0055]

[Table 1]

表 1

	実施例 1	実施例 2	実施例 3	
(A) ポリアミド樹脂 種類	N 6 6	N 6 6	N 6 6	
(B) 膨潤性層状性樹脂 添加量	w t %	0.5	1	1
(C) 銅化合物 ヨウ化銅-銅	w t %	0.02	0.02	0.05
(D) 脂肪酸化合物 エチレンビスステアリルアミド	w t %	0.3	0.3	0.3
(E) 高級脂肪酸金属塩 ステアリン酸カルシウム	w t %	0.03	0.03	0.03
その他 ヨウ化カリウム	w t %	0.03	0.03	0.03
曲げ強度	M P a	118	118	120
曲げ弾性率	G P a	3.1	3.2	3.3
引張クリープ	%	7.1	6.8	6.0
表面外観	○	○	○	

Except not adding comparative example 1 fatty acid compound, after carrying out melt kneading to Nylon 66, and the sheet silicate of swelling nature, a copper compound and higher-fatty-acid metal salt

and obtaining a resin composition like Example 2, shaping and evaluation were performed. The result was shown in Table 2.

[0056] Except not adding a comparative example 2 swelling sheet silicate, after carrying out melt kneading to Nylon 66, and a copper compound, a fatty acid compound and higher-fatty-acid metal salt and obtaining a resin composition like Example 2, shaping and evaluation were performed. The result was shown in Table 2.

[0057] Except not adding comparative example 3 copper compound, after carrying out melt kneading to Nylon 66, and the sheet silicate of swelling nature, a fatty acid compound and higher-fatty-acid metal salt and obtaining a resin composition like Example 2, shaping and evaluation were performed. The result was shown in Table 2.

[0058] Except not adding comparative example 4 higher-fatty-acid metal salt, after carrying out melt kneading of the sheet silicate of swelling nature, a copper compound, and the fatty acid compound to Nylon 66 and obtaining a resin composition like Example 2, shaping and evaluation were performed. The result was shown in Table 2.

[0059]

[Table 2]

表 2

	比較例1	比較例2	比較例3	比較例4
(A) ポリアミド樹脂 種類	N 6 6	N 6 6	N 6 6	N 6 6
(B) 比例性層状硅酸塩 添加量 w t %	1	—	1	1
(C) 銅化合物 ヨウ化銅一銅 w t %	0.02	0.02	—	0.02
(D) 脂肪酸化合物 エチレンビスステアリルアミ w t %	—	0.3	0.3	0.3
(E) 高級脂肪酸金属塩 ステアリン酸カルシウム w t %	0.03	0.03	0.03	—
その他 ヨウ化カリウム w t %	0.03	0.03	0.03	0.03
曲げ強度 MPa	113	103	110	113
曲げ弾性率 GPa	2.9	2.5	2.8	3.0
引張クリープ %	9.2	12.0	10.2	8.8
表面外観	×	○	○	×

[0060]

[Effect of the Invention] In this invention, the resin composition excellent in mechanical properties is obtained easily, especially an inorganic ash content is excellent in rigidity, such as a rate of bending flexibility, and creep property, at least, and the good resin-molding article of mold-goods surface appearance is obtained.

Therefore, it is suitable for mold goods, such as autoparts, an electric electronic component, building materials, furniture, and daily-use products.

[Translation done.]